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1                   **PREPARING A HIGH VISCOSITY INDEX,**  
2                   **LOW BRANCH INDEX DEWAXED OIL**

3           This patent application claims priority from U.S. Provisional Patent  
4   Application Serial No. 60/077070, filed March 6, 1998, the specification of  
5   which is incorporated herein by reference for all purposes.

6                   **BACKGROUND OF THE INVENTION**

7  
8           The present process is a dewaxing process for producing very high  
9   viscosity index, low pour point lubricating oil base stocks from a mineral oil  
10   feed. When preparing a lubricating oil base stock from a mineral oil, viscosity  
11   index is generally increased to a target value during an upgrading step using  
12   hydrocracking, solvent refining, etc. Pour point is generally reduced to a  
13   target value during a dewaxing step, using catalytic or solvent dewaxing. In  
14   conventional processes, the viscosity index generally decreases during  
15   dewaxing, since conventional dewaxing processes remove high viscosity  
16   index wax from the lubricating oil base stock. Improvements in automotive  
17   engine design is putting ever increasing pressure on the quality of motor oils.  
18   Demand for low volatility oils having superior low temperature properties is  
19   increasing, and refiners are constantly looking for new processes to aid them  
20   in meeting current demands.

21           High quality lubricants should be, and generally are, paraffinic in  
22   nature, since paraffins have a high viscosity index. However, normal  
23   paraffins, in particular, are waxy in character, and contribute to a high pour  
24   point in the oil. Conventional processes for removing these normal paraffins  
25   reduce yield of the lubricant, and have a tendency to reduce the viscosity  
26   index of the dewaxed oil. The viscosity index may be increased in the  
27   lubricating oil base stock by addition of viscosity index improvers. However,  
28   viscosity index improvers are expensive, and tend to fragment at conditions of  
29   high temperature and high shear, both of which are commonly found in  
30   modern automotive engines.

31           Synthetic lubricants may be used when very low pour point and very  
32   high viscosity index lubricants are desired. But the starting materials used to

1 make the synthetic lubricants, and the processes used in manufacturing these  
2 lubricants, are very expensive. The need remains for a lubricating oil base  
3 stock, having synthetic-like properties but prepared from a mineral oil feed  
4 using methods which are similar to those presently employed in refinery  
5 processes.

6 A major breakthrough came with the discovery of new dewaxing  
7 catalysts which were found to isomerize rather than crack the wax molecules.  
8 Isomerization alters the molecular structure of wax molecules, and generally  
9 decreases the pour point of the molecule without significantly changing its  
10 boiling point. In contrast to solvent dewaxing and to wax cracking, isomerized  
11 molecules are retained in the lubricating oil base stock, increasing yield of  
12 lubricating oil base stock without reducing viscosity index significantly. A  
13 particularly important group of isomerization catalysts include the  
14 silicoaluminophosphate molecular sieves (SAPO). The preparation of  
15 silicoaluminophosphate molecular sieves, including SAPO-11, SAPO-31 and  
16 SAPO-41, are taught, for example, in U.S. Patent No. 4,440,871. Dewaxing  
17 processes using such molecular sieves are taught in U.S. Patent  
18 No. 4,859,311; U.S. Patent No. 4,867,862; U.S. Patent No. 4,921,594; U.S.  
19 Patent No. 5,082,986; U.S. Patent No. 5,135,638; U.S. Patent No. 5,149,421;  
20 U.S. Patent No. 5,246,566; U.S. Patent No. 5,413,695; and U.S. Patent  
21 No. 4,960,504.

22 SAPO molecular sieves belong to an important class of non-zeolitic  
23 molecular sieve dewaxing catalysts which are useful as isomerization  
24 catalysts for converting wax and wax-like components. Non-zeolitic molecular  
25 sieves are microporous compositions that are formed from  $\text{AlO}_2$  and  $\text{PO}_2$   
26 tetrahedra which form 3-dimensional crystalline structures, and are described  
27 broadly for this use in U.S. Patent No. 4,906,351 and U.S. Patent  
28 No. 4,880,760.

29 These catalysts with isomerization and hydroisomerization activity have  
30 been found to provide a method for preparing very high viscosity index  
31 lubricating oil base stocks from waxy feedstocks in a single reaction step.

1 Producing a  $C_{20}^{+}$  lube oil from olefins, including normal alpha olefins, using an  
2 intermediate pore size molecular sieve and at least one Group VIII metal, is  
3 taught in U.S. Patent No. 5,082,986. In U.S. Patent No. 5,135,638, a waxy  
4 feed containing greater than about 50% wax is isomerized over a catalyst  
5 comprising a molecular sieve having 1-D pores having a minor axis between  
6 about 4.2Å and about 4.8Å and a major axis between about 5.4Å and about  
7 7.0Å and at least one Group VIII metal at a pressure of from about 15 psig  
8 (103 kPa) to about 2000 psig (13.8 MPa). SAPO-11, SAPO-31, SAPO-41,  
9 ZSM-22, ZSM-23 and ZSM-35 are included in U.S. Patent No. 5,135,638 as  
10 intermediate pore size materials which possess the indicated pore geometry.  
11 In U.S. Patent No. 5,282,958, a feed including straight chain and slightly  
12 branched chain paraffins having 10 or more carbon atoms is isomerized with  
13 an intermediate pore size molecular sieve having a defined pore geometry,  
14 crystallite size, acidity and isomerization selectivity. Feeds which may be  
15 processed by the method of U.S. Patent No. 5,282,958 include waxy feeds,  
16 which contain greater than about 50% wax. Such feeds are also taught as  
17 often containing greater than 70% paraffinic carbon. U.S. Patent  
18 No. 5,376,260 is directed to pour point reduction of a heavy oil which contains  
19 naphthenic wax, using SSZ-32. Heavy oils comprising up to 100% wax are  
20 taught.

21 Large pore zeolites represent another class of catalysts which have  
22 been taught for wax isomerization. EP 464546 teaches producing a high  
23 viscosity index lubricant from a petroleum wax feed having a paraffin content  
24 of at least 40 weight percent. The catalyst is a low acidity zeolite  
25 isomerization catalyst having an alpha value of not more than 20. Zeolite  
26 beta which contains boron as a framework component of the zeolite is taught  
27 as being preferred. The catalyst in WO 96/26993 is a low acidity large pore  
28 zeolite isomerization catalyst having a ratio of  $SiO_2/Al_2O_3$ , as synthesized, of  
29 at least 200:1. WO 96/13563 teaches an isomerization process for producing  
30 a high viscosity index lubricant using a low acidity large pore molecular sieve  
31 having a crystal size of less than 0.1 micron, an alpha value of not more than  
32 30 and containing a noble metal hydrogenation component. EP 225053

1 teaches isomerization dewaxing using a large pore, high silica zeolite  
2 dewaxing catalyst, followed by a subsequent dewaxing step which selectively  
3 removes the more waxy n-paraffin components. The selective dewaxing step  
4 may be either a solvent or a catalyst dewaxing, preferably using highly shape  
5 selective zeolite such as ZSM-22 or ZSM-23.

6 While the intermediate pore size molecular sieves have been shown to  
7 be effective for producing high viscosity index lubricating oil base stocks, the  
8 need remains for even higher viscosity index products which have been  
9 dewaxed to a low pour point.

#### 10 SUMMARY OF THE INVENTION

11 An object of the present invention is to provide a process for producing an oil,  
12 having a very high viscosity index and a very low pour point, which is suitable  
13 for use as a lubricating oil base stock. The feedstock to the present process  
14 is a waxy feed which may be derived from mineral oils and mineral oil crudes.  
15 The oil which is produced has lubricating oil properties that approach, and  
16 may exceed, the lubricating oil properties of a synthetic lubricating oil base  
17 stock. Accordingly, the present invention provides a process for preparing an  
18 oil suitable for use as a lubricating oil base stock and having a viscosity index  
19 of greater than 140 and a target pour point of less than or equal to  $-10^{\circ}\text{C}$   
20 comprising:

- 21 a) contacting a waxy feed over a catalyst comprising a molecular sieve  
22 having 1-D pores with a pore diameter of between about 5.0 Å and  
23 about 7.0 Å, and at least one Group VIII metal, at a pressure of from  
24 about 15 psig (103 kPa) to about 2500 psig (13.8 MPa) to produce an  
25 isomerized oil having a pour point of at least  $6^{\circ}\text{C}$  above a target pour  
26 point; and
- 27 b) solvent dewaxing the isomerized oil to produce a lubricating oil base  
28 stock having the target pour point and a viscosity index of greater than  
29 about 140.

30 A particularly preferred molecular sieve useful in the isomerization step  
31 has sufficient isomerization selectivity such that, when contacting a n-C<sub>24</sub> feed

1 at a total pressure of 1000 psig (6.99 MPa), hydrogen flow equivalent to 6.7  
2 MSCF/bbl (1010 std liters H<sub>2</sub>/kg oil), and a feed rate equivalent to 0.6 hr<sup>-1</sup>  
3 LHSV with a catalyst comprising the molecular sieve, to produce a 316°C+  
4 dewaxed product having a pour point of about +20°C and solvent dewaxing  
5 the dewaxed product to a pour point of -15°C or below, an isomerized  
6 product having a branching index of less than about 1.75 is formed.

7 The process is capable of producing an oil having a very high viscosity  
8 index, e.g., greater than about 140 or even greater than about 150. The  
9 process is further capable of producing an oil having a very low pour point,  
10 e.g. less than or equal to about -10°C, or less than or equal to about -20°C, or  
11 even less than or equal to about -30°C.

12 In another embodiment, the present invention provides a unique  
13 lubricating oil base stock, which has a viscosity index of at least about 140,  
14 preferably at least about 150 and more preferably at least about 160, a pour  
15 point of less than or equal to about -10°C, and a viscosity, measured at  
16 100°C, of about 3 cSt or less.

#### 17 IN THE FIGURES

18 Figure 1 shows the benefit of isomerizing a waxy feed with SM-3 and  
19 solvent dewaxing the isomerized oil compared to isomerizing the waxy feed  
20 alone.

21 Figure 2 shows the benefit of isomerizing a waxy feed with SSZ-32 and  
22 solvent dewaxing the isomerized oil compared to isomerizing the waxy feed  
23 alone.

#### 24 DETAILED DESCRIPTION OF THE INVENTION

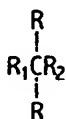
25 Normal paraffins are a major contributor to wax and a high pour point  
26 in a lubricating oil base stock. It is desirable to isomerize the normal paraffins  
27 to low pour point branched paraffins which retain the boiling range of the  
28 normal paraffins from which there were converted.

29 Among other factors, the present invention is based on the discovery  
30 that the number of branches produced while isomerizing a normal paraffin

1 viscosity index which approaches, and can exceed, the viscosity index of  
2 synthetic lubricants having the same viscosity.  
3 As used herein, a normal paraffin, or alkane, is a saturated aliphatic  
4 hydrocarbon containing only --CH<sub>3</sub> and --CH<sub>2</sub>-- groups. A branched paraffin is  
5 a saturated aliphatic hydrocarbon containing one or more



or



6 groups. As used herein, each R represents a branch, where R is an alkyl  
7 independently selected from --CH<sub>3</sub>, --C<sub>2</sub>H<sub>5</sub>, --C<sub>3</sub>H<sub>7</sub>, or --C<sub>4</sub>H<sub>9</sub>, and preferably  
8 from --CH<sub>3</sub> or --C<sub>2</sub>H<sub>5</sub>. R<sub>1</sub> and R<sub>2</sub> represent portions of the paraffin chain or  
9 backbone. Thus, a singly branched paraffin has one R group per paraffin  
10 molecule, a doubly branched paraffin two R groups, a triply branched paraffin  
11 three R groups, etc.

12 The feedstock to the present process is a "waxy feed". The feedstock  
13 will normally be a C<sub>20</sub><sup>+</sup> feedstock, generally boiling above about 316°C and  
14 containing paraffins, olefins, naphthenes, aromatics and heterocyclic  
15 compounds and a substantial proportion of higher molecular weight  
16 n-paraffins and slightly branched paraffins which contribute to the waxy  
17 nature of the feedstock. Hydroprocessed stocks are a convenient source of  
18 stocks of this kind and also of other distillate fractions since they normally  
19 contain significant amounts of waxy n-paraffins.

20 As used herein, the term "waxy feed" includes petroleum waxes.  
21 Exemplary suitable feeds for use in the process of the invention also include  
22 waxy distillate stocks such as gas oils, lubricating oil stocks, synthetic oils and  
23 waxes such as those by Fischer-Tropsch synthesis, high pour point

1 polyalphaolefins, foots oils, normal alpha olefin waxes, slack waxes, deoiled  
2 waxes and microcrystalline waxes. Slack wax is wax recovered from a  
3 conventional solvent dewaxing process. Slack wax can be obtained from  
4 either a straight run gas oil, a hydrocracked lube oil or a solvent refined lube  
5 oil. Hydrocracking is preferred because that process can also reduce the  
6 nitrogen content to low values. With slack wax derived from solvent refined  
7 oils, deoiling can be used to reduce the nitrogen content. Optionally,  
8 hydrotreating of the slack wax can be carried out to lower the nitrogen content  
9 thereof. Slack waxes possess a very high viscosity index, normally in the  
10 range of from 120 to 200, depending on the oil content and the starting  
11 material from which the wax has been prepared. Slack waxes are therefore  
12 eminently suitable for the preparation of lubricating oils having very high  
13 viscosity indices, i.e., from about 140 to about 180. Foots oil is prepared by  
14 separating oil from the wax. The isolated oil is referred to as foots oil.

15 The feedstock employed in the process of the invention preferably  
16 contains greater than about 50% wax, more preferably greater than about  
17 80% wax, most preferably greater than about 90% wax. However, a highly  
18 paraffinic feed having a high pour point, generally above about 0°C, more  
19 usually above about 10°C, but containing less than 50% wax is also suitable  
20 for use in the process of the invention. Such a feed should preferably contain  
21 greater than about 70% paraffinic carbon, more preferably greater than about  
22 80% paraffinic carbon, most preferably greater than about 90% paraffinic  
23 carbon.

24 A catalyst useful in the present process comprises an intermediate  
25 pore size molecular size and a hydrogenation component. Catalysts of this  
26 type are taught in U.S. Patent No. 5,135,638, the entire disclosure of which is  
27 incorporated herein by reference for all purposes. The phrase "intermediate  
28 pore size", as used herein means an effective pore aperture in the range of  
29 from about 5.0 to about 7.0 Å, preferably from about 5.3 to about 6.5Å, when  
30 the porous inorganic oxide is in the calcined form. The effective pore size of  
31 the molecular sieves can be measured using standard adsorption techniques  
32 and hydrocarbonaceous compounds of known minimum kinetic diameters.



1 See Breck, Zeolite Molecular Sieves. 1974 (especially Chapter 8); Anderson  
2 et al., J. Catalysis 58, 114 (1979); and U.S. Pat. No. 4,440,871, the pertinent  
3 portions of which are incorporated herein by reference.

4 In performing adsorption measurements to determine pore size,  
5 standard techniques are used. It is convenient to consider a particular  
6 molecule as excluded if it does not reach at least 95% of its equilibrium  
7 adsorption value on the molecular sieve in less than about 10 minutes  
8 ( $p/p_o=0.5$ ; 25°C).

Intermediate pore size molecular sieves will typically admit molecules having kinetic diameters of 5.3 to 6.5Å with little hindrance. Examples of such compounds (and their kinetic diameters in Å) are: n-hexane (4.3), 3-methylpentane (5.5), benzene (5.85), and toluene (5.8). Compounds having kinetic diameters of about 6 to 6.5Å can be admitted into the pores, depending on the particular sieve, but do not penetrate as quickly and in some cases are effectively excluded. Compounds having kinetic diameters in the range of 6 to 6.5Å include: cyclohexane (6.0), 2,3-dimethylbutane (6.1), and m-xylene (6.1). Generally, compounds having kinetic diameters of greater than about 6.5Å do not penetrate the pore apertures and thus are not absorbed into the interior of the molecular sieve lattice. Examples of such larger compounds include: o-xylene (6.8), 1,3,5-trimethylbenzene (7.5), and tributylamine (8.1). While the effective pore size as discussed above is important to the practice of the invention, not all intermediate pore size molecular sieves having such effective pore sizes are advantageously usable in the practice of the present invention. Indeed, it is essential that the intermediate pore size molecular sieve catalysts used in the practice of the present invention have a very specific pore shape and size as measured by X-ray crystallography. First, the intracrystalline channels must be parallel and must not be interconnected. Such channels are conventionally referred to as 1-D diffusion types or more shortly as 1-D pores. The classification of intrazeolite channels as 1-D, 2-D and 3-D is set forth by R. M. Barrer in Zeolites, Science and Technology, edited by F. R. Rodrigues, L. D. Rollman and C. Naccache, NATO ASI Series, 1984 which classification is

1 incorporated in its entirety by reference (see particularly page 75). Known  
2 1-D zeolites include cancrinite hydrate, laumontite, mazzite, mordenite and  
3 zeolite L.

4 In general, the pores of the molecular sieve have a major axis between  
5 about 5.0 Å and about 7.0 Å, i.e. the pore diameter of the molecular sieve is  
6 between about 5.0 Å and about 7.0 Å. In one embodiment, the preferred  
7 molecular sieves useful in the practice of the present invention have pores  
8 which are oval in shape, by which is meant the pores exhibit two unequal  
9 axes referred to herein as a minor axis and a major axis. The term oval as  
10 used herein is not meant to require a specific oval or elliptical shape but  
11 rather to refer to the pores exhibiting two unequal axes. In particular, the 1-D  
12 pores of the preferred molecular sieves useful in the practice of the present  
13 invention have a minor axis between about 3.9Å and about 4.8Å and a major  
14 axis between about 5.4Å and about 7.0Å as determined by conventional  
15 X-ray crystallography measurements, following the measurement convention  
16 of W. M. Meier and D. H. Olson, *ATLAS OF ZEOLITE STRUCTURE TYPES*,  
17 Butterworth-Heinemann, Third Revised Edition, 1992.

18 The present invention makes use of molecular sieve catalysts with  
19 selected shape selectivity properties. These shape selectivity properties are  
20 defined by carrying out standard isomerization selectivity tests for isomerizing  
21 tetracosane (n-C<sub>24</sub>). The test conditions include a total pressure of 1000 psig  
22 (6.89 MPa), hydrogen flow equivalent to 6.7 MSCF/bbl (1010 std liters H<sub>2</sub>/kg  
23 oil), a feed rate equivalent to 0.6 hr<sup>-1</sup> LHSV and the use of 0.5g of catalyst  
24 (impregnated with 0.5 wt% Pt and sized to 24-42 mesh [0.35 mm – 0.70 mm])  
25 loaded in the center of a 3 feet long (0.91 m) by 3/16 inch (0.48 cm) inner  
26 diameter stainless steel reactor tube (the catalyst is located centrally of the  
27 tube and extends about 1 to 2 inches [2.54-5.08 cm] in length) with alundum  
28 loaded upstream of the catalyst for preheating the feed. The reactor  
29 temperature is adjusted to achieve a pour point of about +20°C in the 600°F+  
30 (316°C) distillation bottoms of the reactor effluent. The 600°F+ (316°C)  
31 distillation bottoms are then solvent dewaxed to a pour point of about -15°C.

1 To account for the extent of isomerization, a branching index is defined  
2 to characterize the average number of branches per C<sub>24</sub> molecule.

3 
$$BranchingIndex = \sum_i i * b_i / b_t$$

4 where b<sub>i</sub> is the amount of paraffins in the product with an "i" number of  
5 branches, and b<sub>t</sub> is the total amount of paraffins in the product (both normal  
6 and branched).

7 The branching index is determined by analyzing a sample of the  
8 product from the standard isomerization selectivity test using carbon-13 NMR  
9 according to the following four-step process. References cited in the  
10 description detail the process steps.

- 11 1. Identify the CH branch centers and the CH<sub>3</sub> branch termination points  
12 using the DEPT Pulse sequence (Doddrell, D.T.; Pegg, D. T.; Bendall,  
13 M.R. *J. Magn. Reson.* **1982**, 48, 323ff.).
- 14 2. Verify the absence of carbons initiating multiple branches (quaternary  
15 carbons) using the APT pulse sequence (Patt, S.L.; Shoolery, J. N. *J.*  
16 *Magn. Reson.* **1982**, 46, 535ff.)
- 17 3. Assign the various branch carbon resonances to specific branch  
18 positions and lengths using tabulated and calculated values  
19 (Lindeman, L. P.; Adams, J. Q. *Anal. Chem.* **43**, 1971 1245ff; Netzel,  
20 D.A. *et.al. Fuel*, **60**, 1981, 307ff.
- 21 4. Quantify the relative frequency of branch occurrence by comparing the  
22 integrated intensity of its terminal methyl carbon to the intensity of a  
23 single carbon (=total integral/number of carbons per molecule in the  
24 mixture). For the unique case of the isopropyl branch, where both  
25 methyl occur at the same resonance position, the intensity was divided  
26 by two before doing the frequency of branch occurrence calculation.

27 All measurements were performed with Varian 300 MHz spectrometers.  
28 In all cases the spectral width was limited to the saturated carbon region,  
29 about 0-80 ppm vs. TMS (tetramethyl silane). 15-25% solutions by weight in

1 chloroform-d1 excited by 45° pulses followed by an 0.8 sec acquisition time.  
2 In order to minimize non uniform intensity data, the proton decoupler was  
3 gated off during a 10 sec delay prior to the excitation pulse and on during  
4 acquisition. Total experiment times ranged from 11-80 minutes. The DEPT  
5 and APT sequences were carried out according to literature descriptions with  
6 minor deviations described in the Varian operating manuals.

7 A catalyst, if it is to qualify as a catalyst of this invention, when tested in  
8 this manner, must convert sufficient normal C<sub>24</sub> paraffin to form an isomerized  
9 product having a pour point of about -15°C or less and a branching index of  
10 less than about 1.75. Non-zeolitic molecular sieves having the characteristics  
11 of an intermediate pore size molecular sieve as described herein are useful in  
12 the present process. Non-zeolitic molecular sieves are microporous  
13 compositions that are formed from AlO<sub>2</sub> and PO<sub>2</sub> tetrahedra. Thus, the  
14 process of the invention may be carried out using a catalyst comprising an  
15 intermediate pore size non-zeolitic molecular sieve and at least one  
16 Group VIII metal. Non-zeolitic molecular sieves are described, for example,  
17 in U.S. Patent No. 4,861,743, the disclosure of which is completely  
18 incorporated herein by reference for all purposes. Non-zeolitic molecular  
19 sieves include aluminophosphates (AlPO<sub>4</sub>) as described in U.S. Patent  
20 No. 4,310,440, silicoaluminophosphates (SAPO), metalloaluminophosphates  
21 (MeAPO), and nonmetal substituted aluminophosphates (ElAPO).  
22 Metalloaluminophosphate molecular sieves are described in U.S. Patent  
23 Nos. 4,500,651; 4,567,029; 4,544,143; 4,686,093 and 4,861,743. Nonmetal  
24 substituted aluminophosphates are described in U.S. Patent No. 4,973,785.

25 Methods for forming a non-zeolitic molecular sieves may be found, for  
26 example, in U.S. Patent Nos. 4,440,871; 4,710,485; and 4,973,785. Non-  
27 zeolitic molecular sieves are generally synthesized by hydrothermal  
28 crystallization from a reaction mixture comprising reactive sources of  
29 aluminum, phosphorus, optionally one or more elements, other than  
30 aluminum and phosphorous, which are capable of forming oxides in  
31 tetrahedral coordination with AlO<sub>2</sub> and PO<sub>2</sub> units, and one or more organic  
32 templating agents. The reaction mixture is placed in a sealed pressure vessel

1 and heated, preferably under autogenous pressure at a temperature of at  
2 least about 100°C., and preferably between 100°C. and 250°C., until crystals  
3 of the molecular sieve product are obtained, usually for a period of from 2  
4 hours to 2 weeks.

5 A silicoaluminophosphate molecular sieve is suitable as an  
6 intermediate pore size molecular sieve for the present process. The  
7 silicoaluminophosphate molecular sieves belong to a class of non-zeolitic  
8 molecular sieves characterized by a three-dimensional microporous  
9 framework structure of  $\text{AlO}_2$  and  $\text{PO}_2$  tetrahedral oxide units with a unit  
10 empirical formula on an anhydrous basis of:



12 wherein "x", "y", and "z" represent the mole fractions, respectively, of silicon,  
13 aluminum, and phosphorus, wherein "x" has a value equal to or greater than  
14 zero (0), and "y" and "z" each have a value of at least 0.01.

15 Catalytic particulates containing at least one of the intermediate pore  
16 molecular sieves SAPO-11, SAPO-31 and SAPO-41 are particularly useful in  
17 the present process. U.S. Patent No. 4,440,871 describes SAPO's generally  
18 and SAPO-11, SAPO-31, and SAPO-41 specifically. The most preferred  
19 intermediate pore size silicoaluminophosphate molecular sieve for use in the  
20 process of the invention is SAPO-11. When combined with a platinum or  
21 palladium hydrogenation component, the SAPO-11 converts the waxy  
22 components to produce a lubricating oil having excellent yield, very low pour  
23 point, low viscosity and high viscosity index.

24 SAPO-11 comprises a silicoaluminophosphate material having a  
25 three-dimensional microporous crystal framework structure of  $\text{PO}_2$ ,  $\text{AlO}_2$  and  
26  $\text{SiO}_2$  tetrahedral units whose unit empirical formula on an anhydrous basis is:



28 wherein "R" represents at least one organic templating agent present in the  
29 intracrystalline pore system; "m" represents the moles of "R" present per mole  
30 of  $(\text{Si}_x\text{Al}_y\text{P}_z)\text{O}_2$  and has a value of from zero to about 0.3, "x", "y" and "z"

1 represent respectively, the mole fractions of silicon, aluminum and  
 2 phosphorous, wherein "x" has a value greater than zero (0), and "y" and "z"  
 3 each have a value of at least 0.01. The silicoaluminophosphate has a  
 4 characteristic X-ray powder diffraction pattern which contains at least the  
 5 d-spacings (as-synthesized and calcined) set forth below in Table I. When  
 6 SAPO-11 is in the as-synthesized form, "m" preferably has a value of from  
 7 0.02 to 0.3.

8 TABLE I

9	10	11	12
	<u>2<math>\theta</math></u>	<u>Interplanar d-spacings (Å)</u>	<u>Relative Intensity, I/I<sub>0</sub></u>
11	9.4-9.65	9.41-9.17	m
12	20.3-20.6	4.37-4.31	m
13	21.0-21.3	4.23-4.17	vs
14	22.1-22.35	4.02-3.99	m
15	22.5-22.9 (doublet)	3.95-3.92	m-s

16 The most particularly preferred intermediate pore SAPO prepared by  
 17 the present process is SM-3, which has a crystalline structure falling within  
 18 that of the SAPO-11 molecular sieves. The preparation of SM-3 and its  
 19 unique characteristics are described in U.S. Patent Nos. 4,943,424 and  
 20 5,158,665. The entire disclosure of each of these patents is incorporated  
 21 herein by reference for all purposes.

22 Another intermediate pore size silicoaluminophosphate molecular  
 23 sieve preferably used in the process of the invention is SAPO-31. SAPO-31  
 24 comprises a silicoaluminophosphate having a three-dimensional microporous  
 25 crystal framework of PO<sub>2</sub>, AlO<sub>2</sub> and SiO<sub>2</sub> tetrahedral units whose unit  
 26 empirical formula on an anhydrous basis is:



28 wherein R represents at least one organic templating agent present in the  
 29 intracrystalline pore system; "m" represents the moles of "R" present per mole  
 30 of (Si<sub>x</sub>Al<sub>y</sub>P<sub>z</sub>)O<sub>2</sub> and has a value of from zero to 0.3; "x", "y" and "z" represent,  
 31 respectively, the mole fractions of silicon, aluminum and phosphorous,

1 wherein "x" has a value greater than zero (0), and "y" and "z" each have a  
 2 value of at least 0.01. The silicoaluminophosphate has a characteristic X-ray  
 3 powder diffraction pattern (as-synthesized and calcined) which contains at  
 4 least the d-spacings set forth below in Table II. When SAPO-31 is in the  
 5 as-synthesized form, "m" preferably has a value of from 0.02 to 0.3.

6 TABLE II

7	8	9	10	11	12	13	14
		<u>2<math>\theta</math></u>	<u>Interplanar</u>	<u>d-spacings (Å)</u>	<u>Relative</u>		
		8.5-8.6		10.40-10.28	m-s		
		20.2-20.3		4.40-4.37	m		
		21.9-22.1		4.06-4.02	w-m		
		22.6-22.7		3.93-3.92	vs		
		31.7-31.8		3.823-2.814	w-m		

15 SAPO-41, also suitable for use in the process of the invention,  
 16 comprises a silicoaluminophosphate having a three-dimensional microporous  
 17 crystal framework structure of PO<sub>2</sub>, AlO<sub>2</sub> and SiO<sub>2</sub> tetrahedral units, and  
 18 whose unit empirical formula on an anhydrous basis is:



20 wherein R represents at least one organic templating agent present in the  
 21 intracrystalline pore system; "m" represents the moles of "R" present per mole  
 22 of (Si<sub>x</sub>Al<sub>y</sub>P<sub>z</sub>)O<sub>2</sub> and has a value of from zero to 0.3; "x", "y" and "z" represent,  
 23 respectively, the mole fractions of silicon, aluminum and phosphorous,  
 24 wherein "x" has a value greater than zero (0), and "y" and "z" each have a  
 25 value of at least 0.01. SAPO-41 has characteristic X-ray powder diffraction  
 26 pattern (as-synthesized and calcined) which contains at least the d-spacings  
 27 set forth below in Table III. When SAPO-41 is in the as-synthesized form,  
 28 "m" preferably has a value of from 0.02 to 0.03.

TABLE III

	<u>2<math>\theta</math></u>	<u>Interplanar d-spacings (Å)</u>	<u>Relative Intensity, I/I<sub>0</sub></u>
4	13.6-13.8	6.51-6.42	w-m
5	20.5-20.6	4.33-4.31	w-m
6	21.1-21.3	4.21-4.17	vs
7	22.1-22.3	4.02-3.99	m-s
8	22.8-23.0	3.90-3.86	m
9	23.1-23.4	3.82-3.80	w-m
10	25.5-25.9	3.493-3.44	w-m

The group of intermediate pore size zeolites useful in the present process include ZSM-22, ZSM-23, ZSM-35, ZSM-48 and SSZ-32. These catalysts are generally considered to be intermediate pore size catalysts based on the measure of their internal structure as represented by their Constraint Index. Zeolites which provide highly restricted access to and egress from their internal structure have a high value for the Constraint Index, while zeolites which provide relatively free access to the internal zeolite structure have a low value for their Constraint Index. The method for determining Constraint Index is described fully in U.S. Pat. No. 4,016,218 which is incorporated herein by reference.

One of the zeolites of the present invention, ZSM-22, is a highly siliceous material which includes crystalline three-dimensional continuous framework silicon containing structures or crystals which result when all the oxygen atoms in the tetrahedra are mutually shared between tetrahedral atoms of silicon or aluminum, and which can exist with a network of mostly SiO<sub>2</sub>, i.e., exclusive of any intracrystalline cations. The description of ZSM-22 is set forth in full in U.S. Pat. No. 4,556,477, U.S. Pat. No. 4,481,177 and European Patent Application No. 102,716 the contents of which are incorporated herein by reference.

As indicated in U.S. Pat. No. 4,566,477, the crystalline material ZSM-22 has been designated with a characteristic X-ray diffraction pattern as set forth in Table IV.



**TABLE IV**  
**Most Significant Lines of ZSM-22**

<u>Interplanar d-spacings (Å)</u>	<u>Relative Intensity (I/I<sub>0</sub>)</u>
10.9 ± 0.2	m-vs
8.7 ± 0.16	w
6.94 ± 0.10	w-m
5.40 ± 0.08	w
4.58 ± 0.07	w
4.36 ± 0.07	vs
3.68 ± 0.05	vs
3.62 ± 0.05	s-vs
3.47 ± 0.04	m-s
3.30 ± 0.04	w
2.74 ± 0.02	w
2.52 ± 0.02	w

It should be understood that the X-ray diffraction pattern of Table VII is characteristic of all the species of ZSM-22 zeolite compositions. Ion exchange of the alkali metal cations with other ions results in a zeolite which reveals substantially the same X-ray diffraction pattern with some minor shifts in interplanar spacing and variation in relative intensity.

Furthermore, the original cations of the as-synthesized ZSM-22 can be replaced at least in part by other ions using conventional ion exchange techniques. It may be necessary to pre-calcine the ZSM-22 zeolite crystals prior to ion exchange. In accordance with the present invention, the replacement ions are those taken from Group VIII of the Periodic Table, especially platinum, palladium, iridium, osmium, rhodium and ruthenium.

ZSM-22 freely sorbs normal hexane and has a pore dimension greater than about 4Å. In addition, the structure of the zeolite provides constrained access to larger molecules. The Constraint Index as determined by the procedure set forth in U.S. Pat. No. 4,016,246 for ZSM-22 has been determined to be from about 2.5 to about 3.0.

Another zeolite which can be used with the present invention is the synthetic crystalline aluminosilicate referred to as ZSM-23, disclosed in U.S. Pat. No. 4,076,842, the contents of which are incorporated herein by

1 reference. The ZSM-23 composition has a characteristic X-ray diffraction  
2 pattern as set forth herein in Table V.

3

TABLE V

4	Interplanar	Relative
5	<u>d-spacings (Å)</u>	<u>Intensity, I/I<sub>0</sub></u>
6	11.2 ±0.23	m
7	10.1 ±0.20	w
8	7.87 ±0.15	w
9	5.59 ±0.10	w
10	5.44 ±0.10	w
11	4.90 ±0.10	w
12	4.53 ±0.10	s
13	3.90 ±0.08	vs
14	3.72 ±0.08	vs
15	3.62 ±0.07	vs
16	3.54 ±0.07	m
17	3.44 ±0.07	s
18	3.36 ±0.07	w
19	3.16 ±0.07	w
20	3.05 ±0.06	w
21	2.99 ±0.06	w
22	2.85 ±0.06	w
23	2.54 ±0.05	m
24	2.47 ±0.05	w
25	2.40 ±0.05	w
26	2.34 ±0.05	w
27		

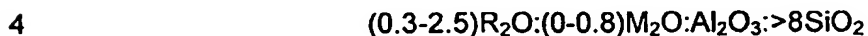
28 The ZSM-23 composition can also be defined in terms of mole ratios of  
29 oxides in the anhydrous state as follows:

30  $(0.58-3.4)M_{2n}O: Al_2O_3:(40-250)SiO_2$

31 wherein M is at least 1 cation and n is the valence thereof. As in the ZSM-22,  
32 the original cations of as-synthesized ZSM-23 can be replaced in accordance  
33 with techniques well-known in the art, at least in part by ionic exchange with  
34 other cations. In the present invention these cations include the Group VIII  
35 metals as set forth hereinbefore.

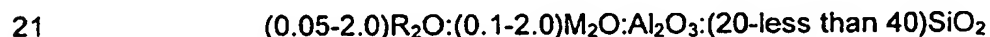
36 Another intermediate pore size zeolite which has been found to be  
37 successful in the present invention is ZSM-35, which is disclosed in U.S.  
38 Patent No. 4,016,245, the contents of which are incorporated herein by  
39 reference. The synthetic crystalline aluminosilicate known as ZSM-35, has a

1 characteristic X-ray diffraction pattern which is set forth in U.S. Pat.  
2 No. 4,016,245. ZSM-35 has a composition which can be defined in terms of  
3 mole ratio of oxides in the anhydrous state as follows:



5 wherein R is organic nitrogen-containing cation derived from ethylenediamine  
6 or pyrrolidine and M is an alkali metal cation. The original cations of the  
7 as-synthesized ZSM-35 can be removed using techniques well known in the  
8 art which includes ion exchange with other cations. In the present invention,  
9 the cation exchange is used to replace the as-synthesized cations with the  
10 Group VIII metals set forth herein. It has been observed that the X-ray  
11 diffraction pattern of ZSM-35 is similar to that of natural ferrierite with a  
12 notable exception being that natural ferrierite patterns exhibit a significant line  
13 at 1.33Å.

14 Another intermediate pore size zeolite which has been found to be  
15 successful in the present invention is SSZ-32, which is disclosed in U.S.  
16 Patent No. 5,053,373, the content of which are incorporated herein by  
17 reference. SSZ-32 has a characteristic X-ray diffraction pattern which is set  
18 forth in U.S. Patent No. 5,053,373. The composition of SSZ-32, as  
19 synthesized and in the anhydrous state, in terms of mole ratios of oxides, is  
20 as follows:



22 where M is an alkali metal cation and R is an organic nitrogen-containing  
23 cation, such as an N-lower alkyl-N'-isopropyl-imidazolium cation. SSZ-32  
24 has a mole ratio of silicon oxide to aluminum oxide in the range of 20 to less  
25 than 40, and has essentially the same X-ray diffraction pattern of ZSM-23.  
26 Hydroconversion processes using SSZ-32 are disclosed, for example, in U.S.  
27 Patent Nos. 5,300,210 and in 5,397,454.

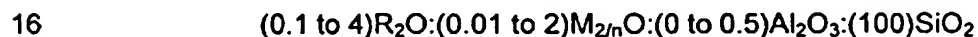
28 ZSM-48 is a crystalline aluminosilicate zeolite which is suitable as a  
29 dewaxing catalyst for the present invention. Zeolite ZSM-48 is disclosed in  
30 U.S. Patent No. 4,585,747, the entire disclosure of which is incorporated

1 herein by reference for all purposes, and has a characteristic X-ray diffraction  
2 pattern as set forth in Table VI.

3 Table VI

4	Interplanar	Relative
5	<u>d-spacings (Å)</u>	<u>Intensity, I/I<sub>o</sub></u>
6	11.8 ± 0.2	s
7	10.2 ± 0.2	w-m
8	7.2 ± 0.15	w
9	4.2 ± 0.08	vs
10	3.9 ± 0.08	vs
11	3.6 ± 0.06	w
12	3.1 ± 0.05	w
13	2.85 ± 0.05	w

14 Zeolite ZSM-48 can also be identified, in terms of mole ratios of oxides and in  
15 the anhydrous state, as follows:



17 wherein M is at least one cation having a valence n and R is the cation. The  
18 cation taught in U.S. Patent No. 4,585,747 is derived from the monomeric,  
19 diquatery compound bis(N-methylpyridyl)ethylinium.

20 Other molecular sieves which can be used with the present invention  
21 include, for example, Theta-1, as described in U.S. Pat. Nos. 4,533,649 and  
22 4,836,910, both of which are incorporated in their entireties by reference,  
23 Nu-10, as described in European Patent Application 065,400 which is  
24 incorporated in its entirety by reference and SSZ-20 as described in U.S. Pat.  
25 No. 4,483,835 which is incorporated in its entirety by reference.

26 X-ray crystallography of SAPO-11, SAPO-31, SAPO-41, ZSM-22, ZSM-23  
27 and ZSM-35 shows these molecular sieves to have the following major and  
28 minor axes: SAPO-11, major 6.3Å, minor 3.9Å; (Bennett, J. M., et al, Zeolites,  
29 1, 160(87)), SAPO-31 and SAPO-41, believed to be slightly larger than  
30 SAPO-11, ZSM-22, major 5.5Å, minor 4.5Å (Kokotailo, G. T., et al, Zeolites,  
31 5, 349(85)); ZSM-23, major 5.6Å, minor 4.5Å; ZSM-35, major 5.4Å, minor  
32 4.2Å. ZSM-48 is a molecular sieve having a 10-ring structure with 1-D pores  
33 having a 5.23 Å major axis and a 5.11 Å minor axis. (Meier, W. M. and  
34 Olsen, D. H., Atlas of Zeolite Structure Types, Butterworths, 1987).

1           It is preferred that relatively small crystal size catalyst be utilized in  
2 practicing the invention. Suitably, the average crystal size is no greater than  
3 about 10 microns (i.e. micrometers), preferably no more than about 5  
4 microns, more preferably no more than about 1 micron and still more  
5 preferably no more than about 0.5 micron.

6           The physical form of the catalyst depends on the type of catalytic  
7 reactor being employed and may be in the form of a granule or powder, and is  
8 desirably compacted into a more readily usable form (e.g., larger  
9 agglomerates), usually with a silica or alumina binder for fluidized bed  
10 reaction, or pills, prills, spheres, extrudates, or other shapes of controlled size  
11 to accord adequate catalyst-reactant contact. The preferred catalyst is in the  
12 form of extrudates with a cross-sectional diameter between about  $\frac{1}{4}$  inch and  
13 about  $\frac{1}{32}$  inch. In the catalyst, the molecular sieve can be composited with  
14 other material resistant to the temperatures and other conditions employed in  
15 organic conversion processes. Such matrix materials include active and  
16 inactive materials and synthetic or naturally occurring zeolites as well as  
17 inorganic materials such as clays, silica and metal oxides. Additional porous  
18 matrix materials include silica, alumina, titania, magnesia and mixtures  
19 thereof. The matrix can be in the form of a cogel. Alumina and silica-alumina  
20 matrix materials are preferred.

21           The intermediate pore size molecular sieve is used in admixture with at  
22 least one Group VIII metal. Preferably, the Group VIII metal is selected from  
23 the group consisting of at least one of platinum and palladium and optionally,  
24 other catalytically active metals such as molybdenum, nickel, vanadium,  
25 cobalt, tungsten, zinc and mixtures thereof. Most preferably, the Group VIII  
26 metal is selected from the group consisting of at least one of platinum and  
27 palladium. The amount of metal ranges from about 0.01% to about 10% by  
28 weight of the molecular sieve, preferably from about 0.1% to about 5% by  
29 weight and more preferably from about 0.2% to about 1% by weight of the  
30 molecular sieve. The techniques of introducing catalytically active metals into  
31 a molecular sieve are disclosed in the literature, and preexisting metal  
32 incorporation techniques and treatment of the molecular sieve to form an

1 active catalyst such as ion exchange, impregnation or occlusion during sieve  
2 preparation are suitable for use in the present process. Such techniques are  
3 disclosed in U.S. Pat. Nos. 3,236,761; 3,226,339; 3,236,762; 3,620,960;  
4 3,373,109; 4,202,996; 4,440,781 and 4,710,485; and in U.S. Application  
5 Serial No. 08/728818; the entire disclosures of which are incorporated herein  
6 by reference for all purposes.

7 The term "metal" or "active metal" as used herein means one or more  
8 metals in the elemental state or in some form such as sulfide, oxide and  
9 mixtures thereof. Regardless of the state in which the metallic component  
10 actually exists, the concentrations are computed as if they existed in the  
11 elemental state.

12 The catalyst may also contain metals which reduce the number of  
13 strong acid sites on the catalyst and thereby lower the selectivity for cracking  
14 versus isomerization. Especially preferred are the Group IIA metals such as  
15 magnesium and calcium. The Group VIII metal utilized in the process of this  
16 invention can mean one or more of the metals in its elemental state or in  
17 some form such as the sulfide or oxide and mixtures thereof. As is customary  
18 in the art of catalysis, when referring to the active metal or metals, it is  
19 intended to encompass the existence of such metal in the elementary state or  
20 in some form such as the oxide or sulfide as mentioned above, and  
21 regardless of the state in which the metallic component actually exists, the  
22 concentrations are computed as if they existed in the elemental state.

23 The catalytic isomerization step of the invention may be conducted by  
24 contacting the feed with a fixed stationary bed of catalyst, with a fixed  
25 fluidized bed, or with a transport bed. A simple and therefore preferred  
26 configuration is a trickle-bed operation in which the feed is allowed to trickle  
27 through a stationary fixed bed, preferably in the presence of hydrogen.

28 The catalytic isomerization conditions employed depend on the feed  
29 used and the desired pour point. Generally, the temperature is from about  
30 200°C to about 475°C, preferably from about 250°C and to about 450°C. The  
31 pressure is typically from about 15 psig ( 103 kPa) to about 2500 psig (27.2

1 MPa), preferably from about 50 psig (345 kPa) to about 2000 psig (13.8  
2 MPa), more preferably from about 100 psig to about 1500 psig (10.3 MPa).  
3 The liquid hourly space velocity (LHSV) is preferably from about  $0.1\text{ hr}^{-1}$  to  
4 about  $20\text{ hr}^{-1}$ , more preferably from about  $0.1\text{ hr}^{-1}$  to about  $5\text{ hr}^{-1}$ , and most  
5 preferably from about  $0.1\text{ hr}^{-1}$  to about  $1.0\text{ hr}^{-1}$ . Low pressure and low liquid  
6 hourly space velocity provide enhanced isomerization selectivity which results  
7 in more isomerization and less cracking of the feed thus producing an  
8 increased yield.

9 Hydrogen is preferably present in the reaction zone during the catalytic  
10 isomerization process. The hydrogen to feed ratio is typically from about 500  
11 to about 30,000 SCF/bbl (standard cubic feet per barrel) (76-4540 std liters  
12  $\text{H}_2/\text{kg oil}$ ), preferably from about 1,000 to about 10,000 SCF/bbl (151-1510 std  
13 liters  $\text{H}_2/\text{kg oil}$ ). Generally, hydrogen will be separated from the product and  
14 recycled to the reaction zone. Strong acidity may also be reduced by  
15 introducing nitrogen compounds, e.g.,  $\text{NH}_3$  or organic nitrogen compounds,  
16 into the feed; however, the total nitrogen content should be less than 50 ppm,  
17 preferably less than 10 ppm.

18 In the dewaxing process using the catalyst of the present invention, the  
19 pour point of the isomerized product is lower than the pour point of the waxy  
20 feed to the dewaxing process. For oils of commercial interest, the pour point  
21 of the oil is generally below about  $10^\circ\text{C}$ , and often below  $0^\circ\text{C}$ . While a low  
22 pour point is desired in the product from the isomerization step, excessive  
23 isomerization has a detrimental effect on product viscosity index, as  
24 described hereinbefore. The wax content of the isomerized oil is between  
25 about 1% and about 40%, preferably between about 3% and about 20%, of  
26 the wax content of the waxy feed. The isomerization step, then preferentially  
27 removes between about 60% and about 99% by weight of the wax contained  
28 in the waxy feedstock. Thus, the pour point of the isomerized product, while  
29 being substantially lower than the pour point of the feed to the isomerization  
30 process, will be at least about  $6^\circ\text{C}$ , and more usually at least about  $12^\circ\text{C}$   
31 above the target pour point set for the finished lubricating oil base stock. The  
32 viscosity index of the isomerized product will be generally above about 140

1 and preferably above about 150. With some products, a viscosity index of  
2 160 or above is possible.

3 The wax content of the oil set forth herein is determined from a  
4 conventional solvent dewaxing method. An example method is as follows:

5 300 g of oil is diluted 50/50 with a 4:1 mixture of methyl ethyl ketone  
6 and toluene which is cooled to  $-20^{\circ}\text{C}$  in a refrigerator. The mixture is filtered  
7 through a Coors funnel at  $-15^{\circ}\text{C}$ . using Whatman No. 3 filter paper. The wax  
8 is removed from the filter and placed in a tared 2 liter flask. The solvent is  
9 removed on a hot plate and the wax weighed.

10 The present integrated two-step process comprises a catalytic  
11 isomerization step and a solvent dewaxing step. Following the isomerization  
12 of the waxy feed, the pour point of the isomerized oil will generally be at least  
13 about  $6^{\circ}\text{C}$  and preferably at least about  $12^{\circ}\text{C}$  above a target pour point of the  
14 finished oil. Continued isomerization results in unselective isomerization and  
15 the formation of increased numbers of triply branched paraffins, resulting in a  
16 reduced viscosity index. Thus, the isomerized oil is solvent dewaxed to a  
17 desired target pour point, which is determined by the particular grade of oil  
18 which is being produced. The target pour point will generally be less than or  
19 equal to about  $-10^{\circ}\text{C}$ . For high quality oils, a pour point less than or equal to  
20 about  $-20^{\circ}\text{C}$  or even less than or equal to about  $-30^{\circ}\text{C}$  may be preferred.  
21 Depending on the dewaxing conditions and the feeds used for the dewaxing  
22 process, a viscosity index above 140 can be achieved. Lubricating oil stocks  
23 will generally boil above  $230^{\circ}\text{C}$  ( $450^{\circ}\text{F}$ ), more usually above  $315^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ).

24 Conventional solvent dewaxing processes which are commonly used in  
25 the preparation of a lubricating oil base stock are suitable for the present  
26 integrated process. Such processes include crystallization of the wax from a  
27 chilled mixture of waxy oil and a solvent such as a blended methyl ethyl  
28 ketone/toluene solvent. The slack wax and/or the foots oil recovered as the  
29 residual oil remaining in the slack wax may be recovered or recycled to the  
30 isomerization reaction zone. The isomerized oil which is the feed to the  
31 solvent dewaxing step of the present process will generally have a pour point



1 of less than about 40°C, and a viscosity index of greater than about 125 and  
2 preferably greater than about 140, and more preferably greater than about  
3 150.

4 Feed to the isomerization process may require pretreatment before it  
5 can be satisfactorily processed in the isomerization step. The pretreatment  
6 steps remove heteroatoms such as nitrogen and sulfur which might poison  
7 the isomerization catalyst, or low viscosity index components such as  
8 aromatics and polycyclic naphthenes. A typical hydrocracking process is  
9 described, for example, in U.S. Patent No. 5,158,665, the entire disclosure of  
10 which is already incorporated by reference.

11 It may further be desired to hydrofinish the dewaxed oil in a mild  
12 hydrogenation process to produce more stable lubrication oils. The  
13 hydrofinishing can be conventionally carried out in the presence of a metallic  
14 hydrogenation catalyst, for example, platinum on alumina. The hydrofinishing  
15 can be carried out at a temperature of from about 190°C to about 340°C and  
16 a pressure of from about 400 psig to about 3000 psig (2.76-20.7 MPa). A  
17 description of a typical hydrofinishing process and catalyst which is useful in  
18 the present process is taught in U.S. Patent No. 5,158,665. Hydrofinishing in  
19 this manner is also described in U.S. Pat. 3,852,207, both of which are  
20 incorporated herein by reference for all purposes.

21 The present process is suitable for preparing very high viscosity index  
22 lubricating oil base stocks having a wide range of viscosities, including base  
23 stocks having a viscosity, measured at 100°C, of 10 cSt or higher. These  
24 base oils have a viscosity index of at least about 140 (preferably at least  
25 about 150 and more preferably at least about 160), and a pour point of less  
26 than or equal to about -10°C (preferably less than or equal to about -20°C,  
27 and more preferably less than or equal to about -30°C). A particularly  
28 important base oil prepared in the present process has a viscosity, measured  
29 at 100°C, of about 3 cSt or less, preferably less than about 3 cSt, and a  
30 viscosity index of at least about 140, preferably at least about 150, and more  
31 preferably at least about 160. This relatively light oil prepared in the present

1 process has a viscosity index higher than that produced even in synthetic oils  
2 having a viscosity, measured at 100°C, of about 3 cSt or less.

3 EXAMPLES

4 Comparative Example A

5 Tetracosane (n-C<sub>24</sub>, purchased from Aldrich), which had a pour point of  
6 +50 C and a viscosity at 100 C of about 2.5 cSt, was isomerized over SM-3  
7 impregnated with 0.5 wt% Pt. The catalyst was pelleted, then crushed to 24-  
8 42 mesh for testing. The catalyst was sulfided in situ prior to testing by  
9 injecting H<sub>2</sub>S through a septum into the hydrogen line ahead of the reactor.  
10 Isomerization was carried out in a continuous feed high pressure pilot plant  
11 with once-through hydrogen gas. Run conditions were 1000 psig total  
12 pressure (6.89 MPa), 0.6 hr<sup>-1</sup>LHSV, and 6.7 MSCF/bbl H<sub>2</sub> (1010 std liters  
13 H<sub>2</sub>/kg oil) At a pour point of -25°C, the viscosity index of the 316°C+  
14 distillation bottoms was 132 (Table VII).

15 Example 1

16 Tetracosane was isomerized over the same Pt/SM-3 catalyst as in  
17 Comparative Example A, but to a pour point of +20 °C. The 316 °C+  
18 distillation bottoms were then solvent dewaxed (SDW) to a pour point of -29  
19 °C. The viscosity index of the oil was 148 (Table VII), much higher (about 18  
20 numbers) than obtained with isomerization only to the same pour point  
21 (Figure I). In addition, the isomerized and solvent dewaxed oil had a much  
22 lower average number of branches per molecule.

TABLE VII  
ISOMERIZATION OF n-C<sub>24</sub> OVER Pt/SM-3 AT  
1000 PSIG (6.99 MPa), 0.6 hr<sup>-1</sup> LHSV,  
AND 6.7 MSCF/BBL H<sub>2</sub> (1010 std liters H<sub>2</sub>/kg oil)

	Comparative Example A	Example 1
Temperature, °C	321	332
n-C <sub>24</sub> Conversion, wt%	99.1	99.6
Yield, Wt%		
C4-	0.5	0.9
C5-82 °C	1.9	2.3
82-177 °C	2.8	3.2
177-316°C	8.2	12.3
316 °C+	86.6	81.3
316°C+ Distillation Yield, wt%	87.4	82.2
Solvent Dewax	No	No
Oil, wt%		Yes
Wax, wt%		65.6
Pour Point Before SDW, °C		32.4
		+20
316°C+ Lube Yield, wt%	86.6	81.3
316 °C+ Lube Inspections		
Pour Point, °C	-15	-25
Cloud Point, °C	-1	-8
Viscosity, 40 °C, cSt	8.636	8.372
100 °C, cSt	2.579	2.507
VI	137	132
		148
Avg. Branches/Molecule	1.83	1.97
		1.63
Simulated Distillation, LV%, °C		
St/5	277/358	294/357
30/50	368/379	368/379
50	384	384
70/90	388/392	388/391
95/EP	392/394	393/394
		304/369
		374/382
		385
		388/391
		392/398

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### Comparative Example B

An extrudate catalyst containing 85 wt% SM-3 sieve and 15 wt% Catapal alumina binder was impregnated with 0.4 wt% Pt and crushed to 24-42 mesh (0.35-0.70 mm). It was used to isomerize a 7.8 cSt heavy neutral slack wax (Table VIII) at 0.5 LHSV hr<sup>-1</sup>, 1000 psig (6.99 MPa), and 8 MSCF/bbl H<sub>2</sub> (1210 std liters H<sub>2</sub>/kg oil). Results are given in Table IX, showing a 144 VI at a pour point of -12°C.

### Example 2

Comparative Example B was repeated, except in this case, the feed was isomerized over the SM-3 catalyst to a pour point of 0°C, followed by solvent dewaxing to -18°C. The viscosity index (143, Table IX) was about the same as in the comparative example, but the pour point was lower. In addition, the cloud point was considerably lower.

TABLE VIII  
INSPECTIONS OF HEAVY NEUTRAL SLACK WAX

Sulfur, ppm	7.0
Viscosity, 100 °C, cSt	7.818
Simulated Distillation, LV%, °C	
St/5	198/371
30/50	392/439
50	476
70/90	522/594
95/EP	628/696

TABLE IX  
ISOMERIZATION OF HEAVY NEUTRAL SLACK WAX  
AT 0.5 hr<sup>-1</sup> LHSV, 1000 PSIG (6.99 MPa),  
AND 8 MSCF/BBL H<sub>2</sub> (1210 std liters H<sub>2</sub>/kg oil)  
OVER Pt/SM-3 CATALYST

	Comparative Example B	Example 2
Temperature, °C	349	332
343°F+ Conversion, wt%	27.4	21.9
Wax Conversion, wt%	100	84.1
Selectivity to Lube, wt%	67.4	72.6
Pour Point before SDW, °C		0
Solvent Dewax	No	Yes
Oil, wt%		86.2
Wax, wt%		13.8
650 F+ Lube Yield, wt%	67.4	61.1
Pour Point, °C	-12	-18
Cloud Point, °C	+9	-17
Viscosity, 40 °C, cSt	41.42	37.50
100 °C, cSt	7.367	6.836
VI	144	143
Simulated Distillation, LV%, °C		
St/5	193/357	226/358
30/50	378/425	377/419
50	464	456
70/90	511/585	500/579
95/EP	617/717	629/747

#### Comparative Example C

An SM-3 catalyst similar to that of Comparative Example B was used to isomerize a hydrotreated 4.5 cSt slack wax (Table X) at 0.5 hr<sup>-1</sup> LHSV, 800 psig total pressure (5.61 MPa), and 3 MSCF/bbl H<sub>2</sub> (454 std liters H<sub>2</sub>/kg oil). Results are given in Table XI, showing a 140 VI at a pour point of -7°C.

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Example 3

Comparative Example C was repeated, except in this case, the feed was isomerized at 1100 psig (7.58 MPa) over the SM-3 catalyst to a pour point of  $-3^{\circ}\text{C}$ , followed by solvent dewaxing to  $-14^{\circ}\text{C}$ . The viscosity index (144, Table XI) was higher than in the comparative example, and the pour point was lower.

TABLE X  
INSPECTIONS OF HYDROTREATED SLACK WAX

Density	0.84 g/cm <sup>3</sup>
Sulfur, ppm	33
Nitrogen, ppm	0.3
Pour Point, °C	+39
Viscosity, 70 °C, cSt	8.120
100 °C, cSt	4.465
Wax, wt%	58.2
<u>Dewaxed Oil Properties</u>	
Pour Point, °C	-8
Cloud Point, °C	-8
Viscosity, 40 °C, cSt	21.82
100 °C, cSt	4.609
VI	130

TABLE XI  
ISOMERIZATION OF HYDROTREATED SLACK WAX  
AT 0.5 hr<sup>-1</sup> LHSV AND 3 MSCF/BBL H<sub>2</sub> (450 std liters H<sub>2</sub>/kg oil)  
OVER Pt/SM-3 CATALYST

	Comparative Example C	Example 3
Temperature, °C	327	327
Pressure, MPa	5.61	7.68
Conversion <371°C, wt%	28.9	23.7
Yields, Wt%		
C4-	2.2	2.0
C5-82 °C	3.8	3.3
180-371 °C	31.7	27.8
371°C+	62.8	67.3
371°C+ Yield, Wt%	62.6	66.8
Pour Point before SDW, °C		-3
Solvent Dewax	No	Yes
Oil, wt%		96
Wax, wt%		4
371°C+ Lube Yield, wt%	62.6	64
Pour Point, °C	-7	-14
Cloud Point, °C	-4	-11
Viscosity, 40 °C, cSt	22.0	21.98
100 °C, cSt	4.746	4.785
VI	140	144
Simulated Distillation, LV%, °C		
ST/5	287/368	294/371
30/50	436/452	738/454
95/99	486/501	488/502





1	TABLE XII			
2	ISOMERIZATION OF n-C <sub>24</sub>			
3	AT 1000 PSIG (6.99 MPa), 0.6 hr <sup>-1</sup> LHSV,			
4	AND 6.7 MSCF/BBL H <sub>2</sub> (1010 std liters h <sub>2</sub> /kg oil)			
5	OVER Pt/SSZ-32 CATALYST			
6				
7		Comparative Example D		Example 4
8	Temperature, °C	307	324	310
9	n-C <sub>24</sub> Conversion, wt%	98.9	99.8	87.9
10				
11	Yields, Wt%			
12	C1-C2	0.3	0.4	0.3
13	C3-C4	4.7	5.4	1.8
14	C5-82 °C	7.4	8.4	2.7
15	82-177 °C	11.9	12.0	2.8
16	177-316 °C	12.2	14.8	8.8
17	316 °C+	63.5	59.0	82.7
18				
19	316 °C+ Distillation Yield, Wt%	64.4	68.5	88.9
20				
21	Solvent Dewax	No	No	Yes
22	Oil, Wt%			86.1
23	Wax, Wt%			11.5
24				
25	Pour Point before SDW, °C			+4
26				
27	316 °C+ Lube Yield, Wt%	63.5	59.0	52.9
28				
29	316 °C+ Lube Inspections			
30	Pour Point, °C	-9	-33	-21
31	Cloud Point, C	+2	-13	-7
32				
33	Viscosity, 40 °C, cSt	8.028	6.414	7.669
34	100 °C, cSt	2.506	2.121	2.445
35	VI	152	143	156
36				
37	Avg. Branches/Molecule	1.60		
38				
39	Simulated Distillation, LV%, °C			
40	St/5	273/333	156/240	218/294
41	30/50	371/383	278/373	373/385
42	50	387	380	389
43	70/90	390/393	383/387	391/394
44	95/EP	393/395	388/391	394/394

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TABLE XIII  
ISOMERIZATION OF n-C<sub>24</sub>  
AT 1000 PSIG (6.99 MPa), 0.6 hr<sup>-1</sup> LHSV,  
AND 6.7 MSCF/BBL H<sub>2</sub> (1010 std liters H<sub>2</sub>/kg oil)

Catalyst	Comparative Example E Pt/B-Beta	Comparative Example F Pt/SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Example 1 Pt/SM-3
Temperature, °C	319	329	324
n-C <sub>24</sub> Conversion, Wt%	95.2	92.4	95.1
Yields, Wt%			
C4-	2.8	0.3	0.2
C5-82 °C	5.4	1.3	0.5
82-177 °C	7.3	2.0	1.7
177-316 °C	16.6	6.7	4.3
316 °C+	67.9	89.7	93.3
316 °C+ Dist. Yield, Wt%	69.0	90.3	92.1
Solvent Dewax	Yes	Yes	Yes
Oil, wt%	86.4	86.1	65.6
Wax, wt%	13.1	11.5	32.4
Pour Point before SDW, °C	+16	+22	+20
316 °C+ Lube Yield, Wt%	58.7	77.2	61.2
316 °C+ Lube Inspections			
Pour Point, °C	-18	-15	-29
Cloud Point, °C	-13	-11	-9
Viscosity, 40 °C, cSt	8.354	8.364	8.313
100 °C, cSt	2.517	2.481	2.556
VI	136	126	148
Avg. Branches/Molecule	1.86	2.02	1.63
Simulated Dist., LV%, °C			
S1/5	298/343	316/360	304/369
30/50	364/375	365/375	374/382
50	381	375	385
70/90	385/389	385/390	388/391
95/EP	390/392	391/392	392/398